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Specific rate coefficients from vibrational overtone activation of 1-methylcyclopropene

by

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Abstract

Laser vibrational overtone activation has been used to investigate the reaction channel competition in the isomerization of 1-methylcyclopropene (MCPene). The vibrational overtone activation of three types of CH stretches (methyl, methlenic and olefinic) in the $5\nu_{\text{CH}}$ and $6\nu_{\text{CH}}$ transitions was initiated and all three products (2-butyne, 1,3-butadiene and 1,2-butadiene) were detected by gas chromatography. Stern-Volmer plots were constructed for the appearance of each individual product and the derived experimental specific rate coefficients were compared to those of RRKM theory. The rate coefficients at high energy were 10% higher than predicted and those at low energy were 60 to 80% high. Product ratios of 1,3-butadiene to 2-butyne were independent of pressure. These ratios were compared to the RRKM ratios. The product yield ratio for the lowest energy photolysis compared well with the RRKM ratio but the two higher energy product yield ratios were approximately 35% lower than the RRKM ratio. The implications of these comparisons are discussed.

Introduction

Vibrational overtone activation of chemical reactions¹ produces activated molecules with well defined internal energies² suitable for gaseous unimolecular reaction studies. This technique has been used to measure the experimental energy specific rate coefficient for many reactions in explorations of the validity of RRKM theory. The vibrational overtone absorption spectrum for many hydrocarbons possesses peaks which fit a simple vibrational progression for each type of CH bond (methyl-in-plane, methyl-out-of-plane, olefinic, methylenic, etc.) in the molecule.³ This fact suggests that the photon excitation energy could localize in one portion of the molecule.

Unimolecular reactions such as ring openings, isomerizations, sigmatropic shifts and dissociations have been investigated using vibrational overtone activation. Collisional deactivation rate constants and specific rate coefficients derived from the Stern-Volmer plots have been compared with theory. The electrocyclic ring-opening of cyclobutene possesses a low reaction barrier (32.9 kcal /mole⁴), facilitating its study by vibrational overtone activation. The 5v_{CH} and 6v_{CH} overtones of methylenic and olefinic bonds were studied in a broad pressure region from 1-700 torr. An initial RRKM calculation using parameters developed to describe thermal activation underestimated the experimental Stern-Volmer specific rate coefficients. The RRKM parameters which fit the overtone data incorporated a looser transition state geometry with five vibrational frequencies lowered from 660 to 450cm⁻¹. The Arrhenius parameters resulting from the "loose" transition state calculation overestimated the thermal rate constant.

Vibrational overtone photochemistry of 1- cyclopropylcyclobutene⁵ discovered no difference in the specific rate coefficient when oscillators were excited on either one ring or the other, thus confirming the assumption that it does not matter how the energy is initially distributed among the molecular vibrational motions. The RRKM behavior of tetramethyldioxetane⁶ and quadricyclane⁷ was also confirmed using vibrational overtone excitation. Overtone excitation has been used to initiate the unimolecular dissociation of t-butylhydroperoxide.⁸ Energy transfer and kinetic parameters determined⁹ by master equation calculations fit experimental results in the low pressure range, but do not explain the large curvature at high pressures. Overtone initiated reactions have also been observed in the liquid phase. For example, proton transfer to D₂O solvent from nitromethane results from vibrational overtone photoactivation of the CH stretch with a quantum yield of 3.1×10⁻⁵.¹⁰

If overtone excitation produces species capable of fluorescence, laser induced fluorescence (LIF) can monitor state specific product yields. The photodissociation kinetics of HONO₂¹¹, HOH¹², HOOH¹³ were studied by OH fragment LIF. Combining infrared optical double resonance techniques with LIF¹⁴ provides spectroscopic access to vibrational combination levels which are not accessible from the ground state. With this method the excitation energies close to the dissociation barrier are accessible allowing an accurate determination of the dissociation energy¹⁴. Overtone spectroscopic parameters including rotation-vibration couplings can be determined using infrared

optical double resonance dissociation. For example, the anharmonicities between the OH and OO stretches and the OH stretch and OOH bend in HOOH have been measured.¹⁵

For the isomerization of methyl isocyanide, wavelengths within the CH stretch band contour were photolyzed to check for rotational or vibrational hot band effects on the experimental specific rate coefficient.¹⁶ By its temperature dependence, a hot band based on the lowest frequency bending mode was confirmed to contribute to the $5\nu_{\text{CH}}$ stretch band contour.¹⁷ However the measured specific rate coefficient for $5\nu_{\text{CH}}$, increased monotonically with increasing energy, showing no hot band effect. The possible explanation of this result is that the specific photolysis energy used fell on part of the band contour where mostly transitions for the CH stretch occurred and did not select transitions for the hot band. In contrast, measured specific rate coefficients for the isomerization of allyl isocyanide, with overlapping absorption peaks for the methyl, methylenic and vinyl CH stretches, did not increase monotonically with increasing energy.¹⁸ This behavior was explained by hot bands, however, the appearance of hot bands has not been confirmed spectroscopically.

Collisional energy transfer parameters can be measured with vibrational overtone activation.^{16, 19, 20} The slope of the Stern-Volmer plot changes with collider gas reflecting the changed energy transfer environment. Ratios of the slopes yield the collisional energy transfer efficiency and the average amount of energy transferred per collision, ΔE , can be determined from master equation simulations of the data. Strong and weak collision models have been developed based on t-butylhydroperoxide dissociation kinetics⁹ and the influence of the energy distribution of reactive molecules and energy transfer parameters on the unimolecular reaction rate has been discussed²¹.

More complicated energy transfer effects can be observed because vibrational energies near the activation barriers can easily be selected with vibrational overtone activation.¹⁶ The barrier acts as a chemical switch since molecules whose energy falls below the barrier through collisional energy transfer no longer react. For example, in the isomerization reaction of methyl isocyanide^{16, 21} the Stern-Volmer plots curve at low pressure. The direction of this curvature depends on which vibrational overtone is used for the photoactivation. The curvature is a result of the competition at the reaction barrier between the collisional energy transfer and the isomerization reaction. The observed curvature occurs in the 1 to 30 torr pressure range since the reaction barrier is low (about 37 kcal/mole²²) and the rate coefficient is high (around 10^8 sec^{-1}). The curvature is a "barrier phenomenon" which will decrease as the photolysis energy increases.

For the present work we have chosen the ring opening reaction of methylcyclopropene (MCPene, **1**), shown in Figure 1, for a vibrational overtone activation study. This reaction produces three products: 2-butyne (**2**), 1,3-butadiene (**3**) and 1,2-butadiene (**4**).²³ At total pressures of 20 torr, the thermal kinetics of this ring opening reaction was investigated²⁴ using MCPene diluted in n-butane to avoid dimerization or polymerization. A common intermediate for all three reaction products was postulated as the cyclopropene ring opens forming a biradical (**5**) which then undergoes one of three possible hydrogen shift reactions to form product. Formation of these products via homogeneous unimolecular reactions has been documented²⁴ with the following activation barriers: 37.8 ± 0.37 kJ/mol, 2-butyne; 42.2 ± 0.7 kJ/mol, 1,3-butadiene; 43.8 ± 1.5 kJ/mol, 1,2-butadiene. The stabilities of these three products have a reversed order with 1,3-butadiene being the most stable (-32.3 kcal/mol), 1,2-butadiene being the least stable (-19.4 kcal/mol) and 2-butyne lying intermediate (-23.5 kcal/mol). Another possible biradical intermediate (**6**) has been suggested which leads to a carbene and subsequent insertion to yield methylenecyclopropane (**7**). MCPane has not been observed as a product in this reaction; however, it is believed that the carbene intermediate does form during thermolysis.

Since **5** and **6** are implicated in this reaction profile perhaps vibrational overtone activation can be used to create a vibrationally excited species which resembles one or the other of these two intermediates. Using selective excitation of a particular CH stretch within the molecule, we may be able to influence the product yield ratios. This report documents the first results in our investigation of the effect of excitation wavenumber on the product yield ratios for this system of three competitive unimolecular reactions. We have studied five different excitation wavelengths ranging over 3800 cm^{-1} in energy. In addition to the 6-0 vinyl CH stretch studied previously,²⁵ we have photolyzed the $6\nu_{\text{CH}}$ methyl and methylenic and $5\nu_{\text{CH}}$ vinyl, methyl and methylenic CH stretches. Using gas chromatography we detect the product yields of all three products separately in order to construct individual Stern-Volmer plots for each product.

The ring opening of MCPene has been studied using vibrational overtone activation^{25, 26} using the 6-0 vinylic CH excitation. Baggott and Law found the measured product yield ratio of 1,3-butadiene to 2-butyne, y_3/y_2 , in the total pressure range of 1 to 5 torr was independent of pressure but smaller than that calculated by RRKM theory. The difference in the experimental and calculated product ratio was attributed to inefficient collisional energy transfer. Unfortunately the value of the calculated ratio was not strongly dependent on the magnitude of ΔE and could not be used to determine the collisional energy transfer parameters. However, a ΔE of -730 cm^{-1} was determined from a master equation fitting of the experimental quantum yield versus pressure. The overall conclusion of this work was that the results at the vinyl excitation behaved according to RRKM theory. Samarasinghe and Snavely²⁶ measured the disappearance rate of MCPene with photolysis into the $6\nu_{\text{CH}}$ vinyl CH stretch and calculated the specific rate coefficient from the Stern-Volmer plot. Their result was $1.66 \times 10^8\text{ sec}^{-1}$ for the reaction.

The overtone spectra of MCPene/MCPane in the $5\nu_{\text{CH}}$ and $6\nu_{\text{CH}}$ transition regions have been previously recorded and assigned by Samarasinghe and Snavely.¹⁹ The large peaks at 13359 cm^{-1} in the $5\nu_{\text{CH}}$ transition and at 15623 cm^{-1} in the $6\nu_{\text{CH}}$ transition were assigned as the methylenic C-H stretch. The two smaller, overlapping peaks to the blue of the methylenic, at 13436 and 13582 cm^{-1} (5-0), and at 15736 and 15893 cm^{-1} (6-0), were assigned as the methyl out-of-plane and the methyl in-plane stretches, respectively. The single peak to the far blue of the 6-0 transition, at 17093 cm^{-1} , was assigned as the olefinic (vinyl) stretch. Figure 2 displays the energy diagram for the overtone activation of 1-methylcyclopropene.

Experimental

1-Methylcyclopropene was prepared according to the procedure developed by Fisher and Applequist.²⁷ Following the synthesis the product was purified using several bulb-to-bulb vacuum distillations. at liquid nitrogen temperature. Further distillation was required to enhance the purity of the methylcyclopropene/methylenecyclopropane mixture using water/ice temperature and collecting the sample at dry ice/isopropanol temperature. The distillate was collected over a 24-48 hour period in these high temperature distillations. This procedure was repeated a second time before storing the product under vacuum at liquid nitrogen temperature.

The identify and relative purity of MCPene including the major contaminant, MCPane, was confirmed by NMR and gas chromatography (GC). Although the absolute purity of the synthesis product was unknown, a close approximation could be assumed by the comparison of peak areas from the GC analysis for reactants and solvents from the synthesis. The final purified mixture was about 95% MCPene, 5% MCPane, and small impurities of tetrahydrofuran, 3-chloro-2-methylpropene, 2-butyne and 1,3-butadiene decreasing amounts in that order.

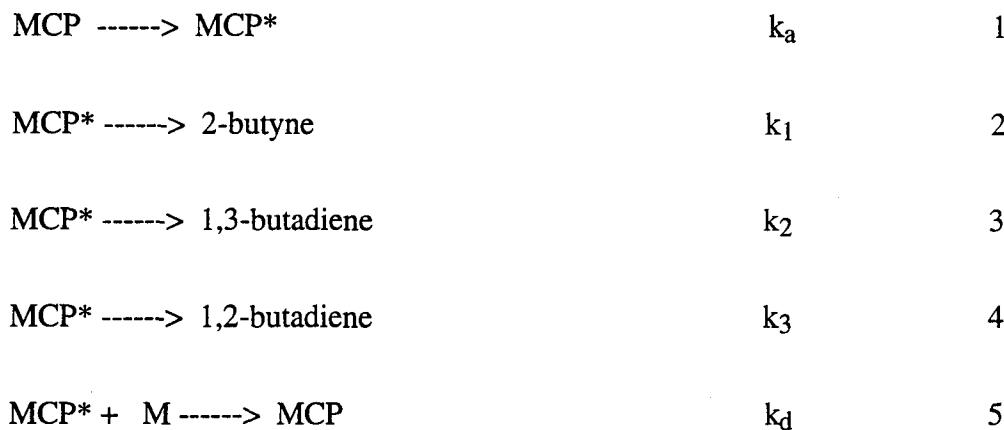
Product analyses were conducted on a Hewlett Packard Gas Chromatograph outfitted with a stainless steel, 30' X 1/8" OD, β,β' -oxydipropiononitrile-bonded porasil column and flame ionization detector. We found a superior separation with this column which increased our sensitivity limits dramatically. For example, the retention times for MCPene: MCPane: 1,3-butadiene: 1,2-butadiene: 2-butyne were 21 \pm 0.5; 26 \pm 0.5; 29 \pm 0.3; 33 \pm 0.3; 47 \pm 1 min. Also in our separation MCPene and MCPane did not overlap. Samples were collected prior to injection onto an evacuated gas sampling loop cooled to liquid nitrogen temperature. Peak areas were quantified using a Hewlett Packard Integrator interfaced to the GC. The intensities of two of the products, 2-butyne and 1,3-butadiene, were calibrated against true standards in order to calibrate the product yields.

For the thermolysis study the starting compounds were collected in a glass sample cell insulated so that temperatures ranging from 100 to 230°C could be achieved. Thermolyses were repeated for various pressures and analyzed by GC.

The photoisomerizations were performed in a glass sample cell with quartz windows set at Brewster's angle. The cell was placed intracavity of a dye laser pumped by an argon laser, and the contents photolyzed for a pre-determined amount of time at constant power. At low pressures (between 0.1 and 2 Torr) photolysis duration was one hour, while at higher pressures, photolyses lasted up to six hours depending on the power output of the dye laser at the photolysis frequency. This procedure was repeated for pressures ranging from 0.1 to 6 Torr. The fourth and fifth vibrational overtones corresponding to the methyl, methylenic and vinyl CH local modes were used in the photolyses. Rhodamine 6G, DCM and pyridine 2 dyes were used for these photolyses.

Results and Discussion

Figures 3 through 8 display the Stern-Volmer plots for the 13359, 13582, 14552, 15623, 15898 and 17093 cm^{-1} photolysis, respectively, for the production of 2-butyne, 1,3-butadiene and 1,2-butadiene. The photolysis at 14552 cm^{-1} corresponds to the $5\nu_{\text{CH}}$ olefinic transition which was observed for the first time in this work. These Stern-Volmer plots were constructed using the kinetic mechanism describing the three competitive reaction channels. The unimolecular reaction of methylcyclopropene produces 2-butyne, 1,3-butadiene and 1,2-butadiene proceeding through the activated complex according to the following equations:



where k_a is the photoactivation rate constant, and k_d is a collisional deactivation constant at a collision frequency at 1 torr. The product formation is described by first-order kinetic equations which are independent of the other channels.

$$\frac{d[P_j]}{dt} = k_j(\varepsilon) [A^*] \quad 6$$

$$Y_{ij} = \frac{(d[A_j]/dt)}{I} \quad 7$$

where P_i is the i -th product concentration, I is the number of absorbed photons and Y_i is the yield of the i -th product. The derivative in equation 6 is constant because the concentration of A^* is constant in terms of the steady-state approximation treatment.

From the above considerations the reaction kinetics can be described using the general form of the Stern-Volmer equation where K_{app} shows the rate of appearance of all three products:

$$\frac{1}{K_{\text{app}}} = \frac{1}{k_a} + \frac{k_d M}{k_a} [k_1(\varepsilon) + k_2(\varepsilon) + k_3(\varepsilon)] \quad 8$$

where M is overall pressure in the reaction vessel. One can see from (6) and (7) that the ratio of $k(\epsilon)$'s is proportional to the ratio of the product yields and, hence, to the ratio of the integrated gas chromatography peaks for the product measurements. Since

$$k_i(\epsilon)/k_j(\epsilon) = Y_i/Y_j = A_i/A_j$$

the following equation can be derived:

$$1/K_{app} = 1/K_a + K_d M A_j / K_a K_j(\epsilon) (\sum A_i) \quad 10$$

This equation describes the j -th channel of the unimolecular reaction. Plotting $1/K_{app}$ versus $M A_j / \sum A_i$ yields the specific rate coefficient for the j -th channel. $M A_j / \sum A_i$ can be interpreted as the partial pressure of the j -th product in the mixture.

These experimental Stern-Volmer plots (figures 3 through 8) appear linear. Plots of this type are expected to curve at low pressure due to the changing competition of reaction and collisional deactivation.⁹ The Stern-Volmer slope is proportional to $k_d / k(\epsilon)$. The experimental value for the slope results from the average over the population distribution of activated molecules. This distribution depends on the total pressure and specific photolysis overtone. If $k_d P$ is approximately equal to $k(\epsilon)$ for the pressure range under study, then as the total pressure changes the Stern-Volmer plot will curve. For most overtone activation experiments the $k(\epsilon)$ is low enough that the curvature would only be observed at pressures much lower than 1 torr. However this curvature has been observed for the overtone activation of methyl isocyanide^{16, 21} since $k(\epsilon)$ for this reaction is large ($4 \times 10^8 \text{ sec}^{-1}$ for the $5v_{\text{CH}}$ transition). The collision frequency is high enough so that even at the lowest experimental pressures (figures 3 through 8) we worked in the "high pressure linear region" (designated as Region 3 in figure 7 of reference 9) since k_d is $8.28 \times 10^6 \text{ torr/s}$ using a hard sphere collisional deactivation model and $k(\epsilon)$ is about 1.2×10^6 to $5 \times 10^6 \text{ s}^{-1}$. With these values the curvature could be expected around 5 torr, simply too low to be experimentally observed.

For vibrational overtone activation in the high pressure Region 3 we assume a simplified activation, reaction and single strong collision deactivation process outlined in equations 1 through 10. With this assumption the Stern-Volmer plots are straight lines with slopes proportional to the collisional deactivation rate constant divided by the specific rate coefficient. Given the linear behavior of our Stern-Volmer plots we have calculated experimental $k(\epsilon)$ values (tabulated as Exp $k(\epsilon)$ in

Table 1) assuming the hard sphere collision frequency. The errors in these slopes are in parentheses after each value and are all below 3%.

An RRKM calculation was undertaken using the RRKM program in Gilbert's UNIMOL suite (Version 1992). The vibrational frequencies were taken from reference 25. We assumed that there was no change in the moment of inertia from reactant to transition state geometry. The internal methyl rotors were not included. The Gilbert program uses a grain size of 100 cm^{-1} for the density of states calculation. The exact count method was used for the density of states. Figure 9 compares these calculated specific rate coefficients to those derived from our Stern-Volmer slopes. The values of $\text{Calc. } K(\epsilon)$ for the specific photolysis energies are also tabulated in Table 1.

The comparison of experimental to theoretical specific rate coefficients is good overall for all three products. For the high energy photolyses the difference is only 10%. However larger differences of 60% and 82% are found for the lower energy photolyses at 13359 and 13582 cm^{-1} , respectively. At these low energies only 2-butyne is produced because the other products possess higher activation barriers. This difference may indicate a problem with the RRKM calculation near the barrier or it may arise from differences in the collisional deactivation with total energy. A complete master equation simulation of the experimental data is required to answer these questions.²⁸

Table 1 Experimental Specific Rate Coefficients compared to RRKM Specific Rate Coefficients

Wavenumber, cm^{-1}	2-butyne		1,3-butadiene		1,2-butadiene	
	Exp. $K(E)$	Calc. $K(E)$	Exp. $K(E)$	Calc. $K(E)$	Exp. $K(E)$	Calc. $K(E)$
13359	$(7.41 \pm 0.12)10^4$	$3.16 \cdot 10^4$	-	-	-	-
13582	$(2.82 \pm 0.04)10^5$	$5.13 \cdot 10^4$	-	-	-	-
14552	$(3.63 \pm 0.08)10^5$	$2.75 \cdot 10^5$	-	-	-	-
15623	$(1.58 \pm 0.01)10^6$	$1.17 \cdot 10^6$	$(1.34 \pm 0.04)10^5$	$1.26 \cdot 10^5$	$(4.78 \pm 0.04)10^4$	$5.25 \cdot 10^4$
15895	$(2.63 \pm 0.02)10^6$	$1.58 \cdot 10^6$	$(3.98 \pm 0.04)10^5$	$3.02 \cdot 10^5$	$(1.48 \pm 0.02)10^5$	$5.62 \cdot 10^4$
17093	$(4.89 \pm 0.05)10^6$	$5.37 \cdot 10^6$	$(1.02 \pm 0.01)10^6$	$1.78 \cdot 10^6$	$(4.68 \pm 0.04)10^5$	$6.03 \cdot 10^5$

The measured specific rate coefficient for the appearance of 2-butyne reported earlier by Snavely and Samarsinghe²⁶ for the 17093 cm^{-1} is much larger than the value reported in this work.

Furthermore the value for the total disappearance of MCPene reported in reference 25 is larger than the one in this work calculated by totalling the product yields in our study. A possible explanation is that our MCPene reactant was 95% pure compared to purities of 61% and 75 % in the other studies. The published spectra in both reference 25 and 26 indicate large methylenecyclopropane impurities. In the GC separations for the current work we could separate completely the MCPene from the MCPane which was not possible in the previous work. Due to this improved analysis, we have a high level of confidence in the current results.

Product yield ratios are independent of the laser power and permit a different type of examination of the product yields. Product yield ratios should vary with energy. These ratios should be independent of pressure in the high pressure limit, referred to as Region 3 above. The experimental product yield ratios for 1,3-butadiene to 2-butyne, y_{13}/y_2 , are plotted versus total pressure in Figure 10. The ratios are independent of pressure. The average values for the experimental y_{13}/y_2 are 0.21, 0.10 and 0.10 for the 17093, 15893 and 15623 cm^{-1} photolysis, respectively. This means that at a lower photolysis energy, less 1,3-butadiene was produced relative to the 2-butyne. This is as expected since the barrier to 1,3-butadiene is higher.

In the case where several products are produced from a common intermediate the product ratios are given by the ratios of the specific rate coefficients for the particular products. The zero pressure product ratios should be close to the ratio of the RRKM rate coefficients at these photolysis energies. Our RRKM product ratios at 17093, 15893 and 15623 cm^{-1} are 0.33, 0.15 and 0.10, respectively. The lower energy methylenic photolysis agrees with the RRKM ratio. For the two higher energy photolyses the product yield ratios do not agree with the theoretical prediction being 35% too low. Part of the difference between the experimental and calculated values is collisional deactivation which decreases the yield of 1,3-butadiene. Another contribution to the difference is the predicted RRKM product yield ratios. Changes in the vibrational frequencies and activation barriers can change these predicted ratios. A master equation with a careful examination of the RRKM calculation should simulate the experimental product yield ratios.²⁸

We believe that at low pressure these product ratio plots should curve. The overall yield of the product with the higher activation barrier should increase at low pressure since at high pressure the collisional deactivation would most likely deactivate it first. All product ratio plots will curve at low

pressure reflecting the increased yield of the product with the higher barrier. For the case of MCPene the curvature occurs at pressures too low to be observed experimentally.

Conclusions

Vibrational overtone activation has been used to study the ring opening reaction of methylcyclopropene to form 2-butyne, 1,3-butadiene and 1,2-butadiene from 0.25 to 6 torr pressure. Six wavelengths corresponding to the olefinic, methylenic and methyl (in plane) CH stretches were chosen for photolysis. These data were collected in the high pressure linear Stern-Volmer region, therefore we determined the experimental specific rate coefficients using a hard sphere collision model. At high energy the experimental values compared well with the RRKM calculated values using only vibrational modes with no rotation or methyl rotors in the calculation. At the lower energies near the activation barrier the experimental values were as large as a factor of 5 too large. A re-examination of the RRKM calculation parameters in conjunction with a full master equation simulation is needed to understand these differences. Experimental product ratios of 1,3-butadiene to 2-butyne were independent of pressure in the range from 1 to 6 torr. The experimental ratios are lower than those predicted by RRKM theory for the higher photolysis energy but agree for the lower energy. The difference between the experimental and calculated values is due to collisional deactivation which decreases the yield of 1,3-butadiene.

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Figure Captions

Figure 1 Reaction of methylcyclopropene to form 2-butyne, 1,3-butadiene and 1,2-butadiene.

Figure 2 Energy (in wavenumbers - cm^{-1}) level diagram for the overtone activation of methylcyclopropene. Numbers in parentheses are in kcal/mole.

Figure 3 Stern-Volmer plot for the photolysis of the methylenic CH at 13359 cm^{-1}

Figure 4 Stern-Volmer plot for the photolysis of the methyl in plane CH at 13582 cm^{-1}

Figure 5 Stern-Volmer plot for the photolysis of the olefinic CH at 14552 cm^{-1}

Figure 6 Stern-Volmer plot for the photolysis of the methylenic CH at 15623 cm^{-1}

Figure 7 Stern-Volmer plot for the photolysis of the methyl in plane CH at 15893 cm^{-1}

Figure 8 Stern-Volmer plot for the photolysis of the olefinic CH at 17093 cm^{-1}

Figure 9 Comparison of RRKM calculated rate coefficients with experiment

Figure 10 Product yield ratios for 1,3-butadiene and 2-butyne

